DEVELOPMENT OF A CO2 SEQUESTRATION MODULE BY INTEGRATING MINERAL ACTIVATION AND AQUEOUS CARBONATION

FINAL TECHNICAL PROGRESS REPORT

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Principal Authors: George Alexander
Parvana Aksoy
John Andrésen
Mercedes Maroto-Valer
Harold Schobert

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Submitting Organization: The Energy Institute
The Pennsylvania State University
204 Research East Building
University Park, PA 16802
Phone: 814 863 1337
Fax: 814 865 9094

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ABSTRACT

Mineral carbonation is a promising concept for permanent CO_2 sequestration due to the vast natural abundance of the raw materials and the permanent storage of CO_2 in solid form as carbonates. The sequestration of CO_2 through the employment of magnesium silicates—olivine and serpentine—is beyond the proof of concept stage. For the work done in this project, serpentine was chosen as the feedstock mineral due to its abundance and availability. Although the reactivity of olivine is greater than that of serpentine, physical and chemical treatments have been shown to increase greatly the reactivity of serpentine.

The primary drawback to mineral carbonation is reaction kinetics. To accelerate the carbonation, aqueous processes are preferred, where the minerals are first dissolved in solution. In aqueous carbonation, the key step is the dissolution rate of the mineral, where the mineral dissolution reaction is likely to be surface-controlled. The relatively low reactivity of serpentine has warranted research into physical and chemical treatments that have been shown to greatly increase its reactivity. The use of sulfuric acid as an accelerating medium for the removal of magnesium from serpentine has been investigated.

To accelerate the dissolution process, the mineral can be ground to very fine particle size, <37 μm, but this is a very energy-intensive process. Previous work in our laboratory showed that chemical surface activation helps to dissolve magnesium from the serpentine (of particle size ≈100 μm) and that the carbonation reaction can be conducted under mild conditions (20°C and 4.6 MPa) compared to previous studies that required >185°C, >13 MPa, and <37 μm particle size. This work also showed that over 70% of the magnesium can be extracted at ambient temperature, leaving an amorphous silica with surface area of about 330 m^2/g. The overall objective of this research program is to optimize the active carbonation process to design an integrated CO_2 sequestration module.

A parametric study was conducted to optimize conditions for mineral activation, in which serpentine and sulfuric acid were reacted. The study focused on the effects of varying the acid concentration, particle size, and reaction time. The reaction yield was as high as 48% with a 5 *M* acid concentration, with lower values directly corresponding to lower acid concentrations. Significant improvements in the removal of moisture, as well as in the dissolution, can be realized with comminution of particles to a D_{50} less than 125 μm. A minimum threshold of 3 *M* concentration of sulfuric acid was found to exist in terms of removal of moisture from serpentine. The effect of reaction time was insignificant. The treated serpentine had low BET surface areas. Results demonstrated that acid concentration provided primary control on the dissolution via the removal of water, which is closely correlated with the extraction of magnesium from serpentine. Single-variable experimentation demonstrated dissolution enhancements with increased reaction time and temperature. An increase in magnesium dissolution of 46% and 70%, relative to a baseline test, occurred for increased reaction time and temperature, respectively.

In addition to the challenges presented by the dissolution of serpentine, another challenge is the subsequent carbonation of the magnesium ions. A stable hydration sphere for the magnesium ion reduces the carbonation kinetics by obstructing the formation of the carbonation products. Accordingly, this research has evaluated the solubility of carbon dioxide in aqueous solution, the interaction between the dissociation products of carbon dioxide, and the carbonation potential of the magnesium ion.

1. INTRODUCTION

1.1. Rationale

Fossil fuels have been the main energy supplier in the United States for over a century. However, the current U.S. fossil energy scenario is undergoing significant transformations, especially to accommodate stringently increasing environmental challenges. The Vision 21 program represents a paradigm shift from traditional power plants by proposing a twenty-first century energy plant that integrates multiple technologies with unprecedented efficiency and no environmental impact, while using a diversified fossil fuel portfolio and opportunity feedstocks to generate electricity, transportation fuels, and chemicals [1]. The greatest challenge to achieve no environmental impact, or zero emissions, is in the area of greenhouse gases, especially CO_2 emissions that are inevitably associated with fossil fuel combustion. Issues related to anthropogenic CO_2 emissions are closely scrutinized by the public, who may demand carbon reduction as a priority for the continuation of large-scale utilization of fossil fuels. Carbon management can be achieved by (i) increasing the efficiency of energy conversion; (ii) using low-carbon or carbon-free energy sources; and (iii) capturing and sequestering CO_2 emissions. It is generally accepted that the first two alternatives will only provide incremental improvements, and, consequently, carbon sequestration technologies must be developed to achieve zero emissions [2].

Anthropogenic emissions have increased CO_2 concentrations in the atmosphere by >30% compared to pre-industrial levels [3]. These anthropogenic additions to atmospheric CO_2 are of growing environmental concern because the energy needs of developed and developing countries are growing at an ever-increasing pace. With fossil fuels currently accounting for 85% of the global energy demand and their prospect to remain at the forefront of the world's energy portfolio, a CO_2 strategy is needed [4]. Further, it is estimated that future global CO_2 emissions will increase from ≈7.4 Gt carbon/year in 1997 to ≈26 Gt carbon/year in 2100 [3,5].

The challenge of stabilizing atmospheric CO_2 levels becomes increasingly difficult as the problem matures. Curtailing these levels in an expeditious manner is advantageous. Therefore there is a clear need to develop carbon sequestration processes. Carbon dioxide sequestration fits into the scheme of decreasing anthropogenic CO_2 emissions. Several options are provided under the CO_2 sequestration umbrella, of which mineral carbonation exists as a geologically stable and benign solution. The mineral carbonation reaction fixes carbon dioxide as a stable carbonate by reaction with calcium- and magnesium-rich minerals. Thus magnesium-rich minerals, such as olivine (Mg_2SiO_4) and serpentine ($Mg_3Si_2O_5(OH)_4$), could react with CO_2 to form geologically stable mineral carbonates, e.g.:

$$(Mg,Ca)_xSi_yO_{x+2y} + x\ CO_2 \rightarrow x\ (Mg,Ca)CO_3 + y\ SiO_2$$

These processes basically mimic the naturally occurring weathering of rocks to form stable magnesium and calcium carbonates. They are exothermic reactions [6]. For serpentine minerals, the reaction can be written as

$$CO_2 + {}^1/_3\ Mg_3Si_2O_5(OH)_4 \rightarrow MgCO_3 + {}^2/_3\ SiO_2 + {}^2/_3\ H_2O$$

and, as written the enthalpy of reaction is –64 kJ/mol [7].

The utilization of magnesium and calcium silicates for the sequestration of carbon dioxide is already beyond the proof-of-concept stage. Research has focused on magnesium- and calcium-bearing minerals because they occur commonly and form stable mineral carbonates. The magnesium-bearing minerals typically contain about 40% magnesium, while calcium-bearing minerals are approximately 10–15% calcium. Thus the focus is on magnesium minerals. The mineral(s) chosen for sequestration need to be in supply commensurate with our CO_2, limiting the options to olivine and serpentine, since they exist in sufficient quantity in accessible deposits [8].

The formation of stable mineral carbonates can occur by the reaction of carbon dioxide with metal ions, such as those of calcium and magnesium. Research has focused on calcium and magnesium silicates due to favorable thermodynamics for carbonation and their relative abundance and availability [8]. Olivine and serpentine react naturally with carbon dioxide, forming magnesium carbonate (magnesite). As shown below, these processes are thermodynamically favored:

$$Mg_2SiO_4 + 2\ CO_2 \rightarrow 2\ MgCO_3 + SiO_2 \qquad \Delta G^o = -209\ kJ/mol$$

$$Mg_3Si_2O_5(OH)_4 + 3\ CO_2 \rightarrow 3\ MgCO_3 + 2\ SiO_2 + 2\ H_2O \qquad \Delta G^o = -67\ kJ/mol$$

Both minerals exist in large quantities and, as shown, with favorable thermodynamics for carbonation. In their native states, olivine is more reactive than serpentine, presumably because the basic building block in the olivine structure is isolated SiO_4^{-4} tetrahedra, as compared to the more strongly linked SiO_4^{-4} tetrahedra in serpentine [9]. Though research continues to be conducted with both minerals, the abundance and wide availability of serpentine make it particularly attractive [10,11]. The natural weathering process is unfortunately limited in extent by slow reaction kinetics. In an effort to expedite the reaction, the use of sulfuric acid as an accelerating medium has been investigated. Based on current CO_2 emission levels, the serpentine requirements for a mineral carbonation plant are not trivial. Therefore, a better understanding of the dissolution of serpentine is warranted. In addition to dissolution studies, the reaction of the magnesium-rich leachate with carbon dioxide presents its own challenges.

Mineral carbonation has several inherent advantages, including a vast natural abundance of the raw materials, the permanent and benign storage of CO_2 in solid form, the overall reaction being exothermic, and the potential of the process being economically viable [4,12]. The key challenge in mineral carbonation is the reaction kinetics, since these naturally occurring processes are extremely slow, on the order of hundreds of thousands of years [13]. The slow kinetics remains an obstacle to large-scale implementation. Accordingly, direct carbonation, in which the minerals react directly with CO_2, has been abandoned in favor of processes in which the minerals are first

dissolved, since the latter have proved to have much faster kinetics than direct carbonation [8,13-15]. During aqueous carbonation, gaseous CO_2 is first dissolved into solution, forming carbonic acid. As the carbonic acid dissociated, the resulting drop in pH facilitates dissolution of magnesium from the magnesium silicate for its subsequent carbonation. Preliminary analysis of this aqueous carbonation scheme has shown that the dissolution of magnesium from the silicate remains inadequate, requiring additional physical or chemical treatments [16].

Serpentine differs from olivine in that it is a hydrated magnesium silicate with about 14% water content [16]. Physical activation, such as a heat-treatment at ≈630°C can remove water from serpentine, in effect activating the serpentine [17,18]. Steam treatment corresponded to a 59.4% conversion to magnesite, compared to 7.2% for the untreated serpentine sample. Although these reported results are encouraging, a high-temperature pretreatment stage is prohibitive due to an excessive energy penalty, 300 kWh/ton [11]. Previous studies have reported that heating serpentine minerals to ≈650°C significantly increases their carbonation reactivity, probably due to dehydroxylation, increase in the surface area, and destabilization of the crystal structure [19,20]. However, this pretreatment is very energy-intensive, requiring about 200 kWh/ton of serpentine or, in other words, a 20% energy penalty for a coal-fired power plant [13]. Chemical routes have been proposed in an effort to avoid the cost-prohibitive heat-treatment.

Previous studies have also focused on crushing magnesium-rich minerals, such as serpentine and olivine, to <37 μm to promote the surface reactions that are known to control most mineral dissolution [21]. These reactions require extensive comminution of the raw minerals, high partial pressures (>13.6 MPa), and long reaction times (>6 hours). Further, all of these operations are very energy-intensive. For example, pilot-scale comminution tests to grind serpentine minerals to –200 mesh (<75 μm) reported an energy penalty of 11.5 kWh/ton of mineral processed [22].

The promotion of mineral carbonation has been investigated with an array of chemicals. If the rate-limiting step in the aqueous carbonation scheme is the action of

carbonic acid removing the magnesium or calcium, then the production of carbonates could be accelerated via a dissolution stage.

Lackner et al. studied the indirect carbonation of magnesium from serpentine using hydrochloric acid as a leaching agent [18]. The resulting hydrated magnesium chloride, $MgCl_2 \cdot 6H_2O$, is then heated to 250°C. Water is driven off first, followed by HCl. The additional chlorine is separated upon hydration of the Mg(OH)Cl, whereupon the carbonation of $Mg(OH)_2$ can take place. Hydrochloric acid leaching enhances the liberation of magnesium, but the amount of energy required to produce $Mg(OH)_2$ limits its applicability [23].

Since the quantity of reactive magnesium is the limiting reagent, Park et al. have studied various solvents to increase the dissolution of magnesium, [24]. Complexing agents were used to polarize and weaken the magnesium bonds in the serpentine structure and to increase solubility. The complexing agents tested were not as successful in terms of dissolution as was hydrochloric acid (used as a reference solvent), with the sole exception of a combination of orthophosphoric
acid, oxalic acid, and ethylenediaminetetraacetic acid (EDTA). This mixture yielded magnesium ion concentrations 1.5 times higher than achieved with hydrochloric acid.

Using acetic acid as an accelerating medium produced calcium extraction of 48% over the course of 250 minutes, but the precipitation reaction only reached about 20% of the theoretical value [25]. The disparity was accounted for by the re-dissolution of calcium carbonate via the dissociation of carbonic acid.

Thus mineral carbonation will only become a viable, cost-effective sequestration technology through innovative development of fast reaction routes under milder regimes in a continuous integrated process [26]. The novel active carbonation concept proposed in Phase 1 of this project utilized surface activation to accelerate the carbonation reaction efficiency. The objective of Phase I was to increase significantly the reaction rates and efficiencies for forming carbonates from minerals, and allowing the integration of

synergistic features for the development of a cost-effective sequestration technology, including acceleration of carbonation efficiency without extensive mineral particle comminution and without heat treatment, while reducing the temperature and pressure conditions of the carbonation reactions.

Several acids—acetic, hydrochloric, phosphoric, and sulfuric—and sodium hydroxide were studied by our group [27]. Phase I of this project showed that the surface area of the raw serpentine, which is about 8 m^2/g, can be increased through physical and chemical activation methods nearly to 330 m^2/g [28]. This was the most effective treatment. Although the reacted serpentine solid did not carbonate, the leachate was susceptible to carbonation under relatively mild conditions. The dissolution reaction was

$$Mg_3Si_2O_5(OH)_4 + 3\ H_2SO_4 \rightarrow 3\ Mg^{+2} + 3\ SO_4^{-2} + 2\ SiO_2 + 5\ H_2O$$

Titration of the magnesium-rich solution with sodium hydroxide yields magnesium hydroxide:

$$Mg^{+2} + SO_4^{-2} + 2\ NaOH \rightarrow Mg(OH)_2 + Na_2SO_4$$

The aqueous carbonation of magnesium hydroxide can then be carried out under milder operating conditions, with a reduction in temperature and pressure from 185°C to 20°C and from 13 MPa to 4.7 MPa:

$$Mg(OH)_2 + CO_2 + H_2O \rightarrow MgCO_3 + 2\ H_2O$$

Because sulfuric acid was the most effective reagent in the dissolution of magnesium (>70%) from serpentine and in producing a high-surface-area silica byproduct, we concentrated on further evaluation of the dissolution of serpentine via sulfuric acid treatment.

Several studies reveal that individual variables and combinations of variables, beyond a critical level, tend to control the dissolution process [29,30]. After an intensive grinding stage of 240 minutes, extraction of magnesium was virtually independent of reaction time and sulfuric acid concentration, and temperatures could remain low while still extracting over 90% of the magnesium from serpentine. With temperatures around 100°C, magnesium extractions approach >90% with 4 *M* sulfuric acid concentrations and 8-hour reaction times.

Previous studies have shown that the carbonation reaction is terminated when the reactive surface of the mineral is either depleted, or becomes inactive by mass-transfer resistance, or both [31]. Therefore, the proposed active carbonation concept aimed to increase the exposure of the reactive surface, and hence accelerate the carbonation reactions, presumably by orders of magnitude. Low-temperature dehydroxylation prior to carbonation can cause the formation of porous intermediate materials with enhanced reactivities [19]. The mineral dissolution reaction is likely to be surface-controlled, and the formation of silica-enriched zones could indicate that the reaction is diffusion-controlled [16]. Further, the formation of silica rims on the reaction surfaces of the minerals may slow the magnesium dissolution [32].

In Phase I of this project, several activation methods were investigated, including physical activation with steam, and chemical activation using a suite of acids and bases. Chemical activation was more effective than physical activation in terms of increasing the surface area, since steam-activated (at 650°C) had serpentines had surface areas only up to 17 m^2/g. Steam-activated serpentine had a 73% conversion to magnesite at 155°C and 13 MPa after 1 hour reaction, while under the same operating conditions the parent sample had only 8% conversion. But, heat treatment is very energy-intensive, and therefore this steam activation route was not considered further. For chemical activation, the most effective acid was sulfuric, which resulted in surface areas of over 330 m^2/g, and more than 70% of the magnesium was dissolved from 100 μm serpentine, i.e., made available for carbonation. Consequently, the subsequent carbonation could be conducted at ambient temperature and low pressure (4.2 MPa). It was possible to achieve 73%

conversion in three hours. This is a significant improvement over previous studies that required temperatures >185°C and pressures of ≈13.6 MPa, as well as extensive comminution (<37 μm) [21,32].

Magnesium extraction is of prime importance because the stoichiometry reveals a 2:1 ratio of serpentine to CO_2, and possibly in the range of 6:1 or even 8:1 [13]. Therefore it is critical to extract the greater part of the magnesium content so as not to drive the ratio further upwards. Over 90% of the magnesium could be extracted, but with any extreme conditions (e.g., severe grinding, high temperatures, and high acid concentrations) individual contributions from other variables tend to be masked [29,30]. Although the reaction variables—acid concentration, particle size, reaction time, and temperature—will have various degrees of control on the dissolution stage, other variables with lesser roles may provide an opportunity to reduce the severity of reaction conditions. Thus, we sought to elucidate the effects of reaction variables under milder conditions.

1.2. Program Objectives

The overall objective of the research program was to optimize the active carbonation process developed in Phase I to design an integrated CO_2 sequestration module for Vision 21 plants. Chemical surface activation helps to dissolve magnesium from serpentine minerals. Furthermore, the carbonation reaction can be conducted at ambient temperature and mild pressure conditions. The module would consist basically of two integrated units for activation and carbonation processes. In the activation unit, serpentine would be mixed with sulfuric acid to activate the mineral. During activation, magnesium is extracted from the serpentine and forms a Mg^{2+} solution that is sent to the carbonation reactor. During the extraction, a high-surface-area (>300 m^2/g) SiO_2-rich solid is precipitated. In the carbonation reactor, CO_2 that has been separated from the flue gas of a power plant would react with the Mg^{2+} solution to precipitate $MgCO_3$. The sulfuric acid would be regenerated and recycled.

1.3. Research Design

This program was divided into four tasks. Task 1, mineral activation, was intended to conduct a parametric study to optimize the conditions for mineral activation, in which serpentine and sulfuric acid are reacted. The optimization of these parameters would yield a maximum dissolution of magnesium and produce a high-surface-area SiO_2 solid as byproduct. Task 2, aqueous carbonation, was intended to react the extracted magnesium with CO_2 at various temperatures and pressures to optimize the variables (temperature, pressure, pH, and stirring speed) that affect carbonation reactions. Task 3, integration of the activation and carbonation units into a CO_2 sequestration module, was aimed at integrating the two reactors—activation and carbonation—and their optimum operating conditions into a module. Task 4 was planned to conduct an assessment of the economic viability of the proposed CO_2 sequestration module. Only Tasks 1 and 2 were completed.

2. EXECUTIVE SUMMARY

Mineral carbonation is a promising concept for permanent CO_2 sequestration due to the vast natural abundance of the raw minerals needed and to the storage on CO_2 in solid form as carbonates. The primary drawback is the kinetics. To accelerate the reaction, aqueous carbonation processes are preferred, in which the minerals are first dissolved into solution. The key step is the dissolution rate of the mineral, a process that is likely to be surface-controlled. To accelerate dissolution, serpentine can be ground to fine particle size (<37 μm), but this is a very energy-intensive process. Alternatively, magnesium could be chemically extracted into aqueous solution. Phase I showed that chemical surface activation helps to dissolve magnesium from ≈100 μm serpentine and that the carbonation reaction can be conducted under conditions—20°C and 4.6 MPa—much milder than those of previous studies (e.g., <37 μm, >185°C, >13 MPa). Phase I also showed that over 70% of the magnesium can be extracted at ambient temperature, leaving amorphous SiO_2 with surface areas of ≈330 m^2/g. The increase in surface area is particularly important because the extraction process only occurs on the surface.

The overall objective of this program was to optimize the active carbonation process developed in Phase I, to design an integrated CO_2 sequestration module. The module consists of two units, for the activation and carbonation processes. In the activation unit, serpentine is mixed with sulfuric acid to activate the mineral. During activation, magnesium is extracted from the serpentine mineral and forms a Mg^{2+} solution that would be sent to the carbonation reactor. During this extraction process, a high-surface-area SiO_2-rich solid would form and be precipitated. In the carbonation reactor, CO_2 that has been separated from the flue gas of a power plant would be reacted with the Mg^{2+} to precipitate $MgCO_3$. The sulfuric acid will be regenerated and recycled to the activation reactor.

Task 1, mineral activation, focused on a parametric study to optimize the conditions for the activation, where serpentine and sulfuric acid were reacted. The study focused on varying the acid concentration, particle size, and reaction time. A particle size reduction to a D_{50} ≤125 μm was necessary for enhancement of dissolution. An increase in acid concentration led to an increase in the mass removal from serpentine, primarily due to magnesium dissolution. Concurrently, there was an increase in surface reactivity through the removal of hydroxyl groups. Acid concentrations ≥3 *M* were favorable. Reactions were indifferent to reaction time at short time intervals. A 24-hour reaction provided a 46% improvement in extraction of Mg^{2+}. Increasing reaction temperature from 25° to 50°C provided a 70% improvement in dissolution.

An interesting tie between reaction time and low surface area was uncovered. This tie may be through oxidation of the serpentine surface or via sulfate crystallization. Multi-stage leaching provided little gain in Mg^{2+} extraction, regardless of whether two stages of acid leaching, or two stages of acid leaching with an intermediate stage of base leaching was used.

The carbonation reaction requires a careful balance of reaction variables. Magnesite is vulnerable to dissolution in an acidic environment. A partial pressure of 4.6 MPa resulted in conditions too acidic for the formation of magnesium carbonates. The bicarbonate ion concentration remains two orders of magnitude too low without addition of a buffer, e.g., sodium bicarbonate, even at lower partial pressures. It is sodium bicarbonate that is responsible for the formation of carbonates.

Thermodynamic calculations provide the range of theoretically favorable reaction conditions for the precipitation of magnesite. However, at these conditions kinetics dictate the predominance of metastable phases over the stable phase, magnesite. Electrostatic interactions between the magnesium ions and water molecules lead to a stable solvation shell. Consequently, the requisite interactions between magnesium ions and carbonate ions are inhibited, leading to prolonged carbonation times and metastable products such as nesquehonite, hydromagnesite, and lansfordite.

The stable hydrated magnesium ion can be affected to promote ligand exchange. Increased reaction temperatures can reduce the hydration number and increase the water exchange rate, both of which improve the chances of bicarbonate or carbonate ions interacting with magnesium ions. Also improving on these interactions is the addition of sodium chloride, reducing the volume of water required to equalize the electronegativity of the magnesium ions. The production of magnesite may not be kinetically favored, but the kinetic limitations may be overcome or at least improved upon by carefully targeting the waters of hydration.

3. EXPERIMENTAL SECTION

3.1 Materials

Serpentine samples from the Cedar Hills quarry in southeastern Pennsylvania were used in this work. The samples were provided by the Department of Energy Albany Research Center. The samples consist of a –4 mm head sample and a –37.5 μm ground sample that had undergone magnetic separation in a separate pilot-plant study conducted elsewhere [33]. In house, a 4.75-L batch ball mill with a ball charge of 30% was used for further sample preparation. Samples of 1500 g of serpentine were ground for 9 minutes on a drive roll. The ground serpentine was sieved to 150–300 μm, 75–150 μm, 37.5–75 μm, and –37.5 μm. The separate size fractions were then wet-separated with a hand magnet to remove magnetite, which is known to form a passivating layer over the serpentine [16]. Analyses of chemical composition were carried out on a Leeman Labs model PS3000UV inductively coupled plasma atomic emission spectrometer. Samples were dissolved using a lithium metaborate fusion technique.

3.2. Statistical Design of Experiments

A Taguchi design of experiment, using the MINITAB® software package, was used to evaluate an optimum combination of control factors. The factors of interest were sulfuric acid concentration, particle size, reaction time, and temperature. To provide a balanced design, where no factor is weighted disproportionately, temperature variations were carried out on optimization of concentration, particle size, and time. The orthogonal array of these three factors at multiple levels provides a balanced design.

3.3. Activation Studies

Chemical activation was carried out on 50-g samples of serpentine, ground to the size fractions mentioned above. The serpentine was reacted in 500 mL of sulfuric acid at prescribed concentrations for predetermined times, as determined by the Taguchi design [34]. The samples were filtered and dried overnight at 105°C. These dissolution experiments were carried out to investigate the relative effects of three factors—acid

concentration, particle size, and reaction time—at three prescribed and distinct levels for each factor. The median particle sizes were selected to be 163, 125, and 63 μm, to be reacted in 500 mL of 1.5, 3, and 5 *M* concentrations of sulfuric acid for 1, 3, and 6 hours.

3.4. Sample Characterization and Analytical Methods

Particle size analysis for the individual size fractions was completed on a Malvern Mastersizer S instrument, using laser scattering coupled with Mie theory and Fraunhofer analysis.

Analyses of chemical composition of both solids and solutions were carried out on a Leeman Labs model PS3000UV inductively coupled plasma (ICP) spectrometer. Solid samples were dissolved prior to analysis using a lithium metaborate fusion technique. Loss-on-ignition (LOI) values were determined by measuring the weight loss after heating at 900°C for 12 hours.

Thermogravimetric analyses (TGA) were conducted using a Perkin-Elmer TGA-7 instrument. Analysis conditions were at atmospheric pressure under nitrogen, with the temperature increased incrementally from 25°C to 900°C at 10°C per minute. X-ray diffraction analyses were conducted with a Philips Analytical 1050 diffractometer with a Hilton Brooks X-ray generator. Scanning electron microscopy images were obtained on an FEI Quanta 600 instrument with magnifications of 120X, 234X and 500X.

A Micrometrics Gemini BET was used to measure the specific surface areas of the parent and acid-treated samples. Adsorption isotherms at relative pressures (P/P_o) of 0.05–0.25 were carried out under liquid nitrogen at 77 K.

3.5. Carbonation Experiments

Carbonation experiments were carried out in a 300-mL Parr model 4561 stirred reactor. Two sets of carbonation experiments were conducted. Pressurized experiments were carried out in the Parr stirred reactor after being purged three times at 0.35 MPa to remove the air from the reactor. In addition, carbonation reactions were also conducted

with a simplified solution of magnesium sulfate heptahydrate and sodium bicarbonate under ambient conditions in 200 mL beakers.

4. RESULTS AND DISCUSSION

4.1.Particle Size Characterization

Particle size analysis was carried out on each of the different size fractions to ensure that, indeed, the desired sizes were prepared. This was confirmed [34,35]. Thus, in the discussion that follows the various size fractions will be referred to by their median particle size, or D_{50}.

For each of the particle size fractions, 25–40% of the particles are beyond the intended sieve fraction limits. Several anomalous, large particles may be responsible for eclipsing the remaining distribution by weighting the upper end of the respective size fractions. Additionally, variation between particle size analysis by sieving and laser light scattering, especially with elongated serpentine particles, can account for the disparity. Results regarding particle size remain informative, as the disparities are internally consistent.

4.2. Magnesium Dissolution

Sulfuric acid has been determined to be an effective agent in the dissolution of magnesium from serpentine for its subsequent carbonation [36]. A selection of acid concentrations was used, ranging from the stoichiometric equivalent to a molar excess of acid. After reaction, the yield was calculated from dividing the weight of the treated and dried filter cake by the initial weight of the serpentine sample. The dissolution of serpentine (or reaction yields) increases with higher acid molar concentrations. An evaluation of particle size dependence shows that the benefits of grinding are realized at <75μm. An increase in temperature from room temperature to 50°C yielded a 70% increase in magnesium dissolution.

The design of experiments yielded a wide range of values of magnesium extraction, for individual experiments ranging from 16.5% to 58.5%, and mean extractions ranging from 20.8% (at 1.5*M* acid concentration) to 48.7% (at 5*M* acid). Variations in the extraction yield were observed with reaction time, particle size, and,

most significantly, with sulfuric acid concentration. (Temperature was held constant, at room temperature, in these experiments.) Our extraction yields are comparable to those of Park et al., who have demonstrated magnesium extractions of 40% under similar conditions of 70°C, 5 hours, but with 1*M* hydrochloric acid, rather than sulfuric acid [24].

Dutrizac et al. used a 7*M* HCl leaching stage at 95°C [37]. Their primary investigations were conducted on serpentine disks, for which they found reaction or extraction depths to be between 300 and 400 μm. They also conducted experiments on serpentine particles less than 600 μm diameter. Not surprisingly, dissolution was independent of particle size below 600 μm. Our studies of particle size dependence show that the benefits of grinding serpentine can be realized at a median particle size below 163 μm, demonstrating the benefits of particle size reduction under our milder conditions. Particle size reduction has a two-fold effect on dissolution: the reactivity is greatly increased as structural defects are imparted into the crystal lattice, and the exposure of reactive magnesium is increased due to an increase in the external surface area.

Based on ICP-AES results, the elemental composition of the ground serpentine varies among size fractions, due to differences in grindability. Additionally, the smallest particle size fraction has the lowest iron concentration. This is of interest for the subsequent carbonation reactions, since as magnetite oxidizes, the carbonation of serpentine is inhibited due to the formation of a passive surface layer of hematite [31]. Not only is liberated magnetite easily removed from the samples, but also a reduction in serpentine losses is achieved, because the parent sample is less likely to be carried away with the magnetite fraction as the extent of comminution increases.

These results were independent of reaction time. To further test the effect of reaction time, an experiment was performed for 24 hours at room temperature, 2*M* sulfuric acid, and <37 μm particle size. Except for reaction time, this is otherwise similar to the 6-hour "baseline" experiment we describe below. The 24-hour reaction time produced a 46% improvement in Mg^{2+} extraction relative to the baseline. For

comparison, Kosuge et al. found that leaching with 3*M* sulfuric acid required three to five times the amount of reaction time to achieve comparable magnesium dissolution as 4 or 5*M* acid [30].

The acid concentration provided the largest degree of control on magnesium dissolution. The dissolution of serpentine increases directly with increased acid concentrations. As the acid concentration increases, so does the degree of protonation. It is thought that a lone pair of electrons on the oxygen atoms in the serpentine structure undergoes protonation as the proton concentration increases. The protonation of the oxygen atoms polarizes and weakens the Mg–O–Si bonds, thereby facilitating removal of the magnesium atoms from the crystal lattice [38]. A 5*M* acid concentration was most effective in removing magnesium. ICP studies confirmed that most of the mass loss from the serpentine could be accounted for by magnesium. Also, ICP analysis of the solid showed that the lowest particle size fractions had the lowest iron concentration. This is important because, as magnetite oxidizes during carbonation, the carbonation of the serpentine is inhibited due to the formation of a passive surface layer of hematite [31].

Experimentation was carried out to investigate multi-stage leaching and increased reaction time and temperature. The baseline experiment was performed at 6 hours, room temperature, 2*M* sulfuric acid concentration, and <37 μm particle size. The particles were kept to this small size fraction to assess the sensitivity of the serpentine to various parameters. It is assumed that similar trends will be seen within larger particles, though they may likely be subdued. For this baseline experiment, the leachate contained 7125 ppm Mg^{2+} (by ICP analysis).

Two-stage leaching tests were conducted by first reacting the solids with sulfuric acid as above, then filtering the solution and rinsing the solids until a neutral pH was obtained. The solids were dried overnight at 105°C, then treated with an additional dose of sulfuric acid, followed by the same rinsing and drying procedure. An experiment with two 2*M* leaching stages produced an additional 1800 ppm Mg^{2+} in the second stage. In a companion experiment in which 1*M* sulfuric acid was used in both stages, the yields were

6200 ppm and 1500 ppm Mg^{2+} in the first and second stages, respectively. The two-stage leaching tests were conducted to determine whether the thermodynamic solubility of the magnesium ions was being approached and the concentration of magnesium ions in solution was inhibiting the further dissolution of magnesium. It appears that a two-stage process provides only a narrow improvement, as the secondary stage resulted in relatively small additional Mg^{2+} when compared to the baseline test.

A surprising result was the lack of a trend for increasing magnesium removal with increasing time. An experiment at a reaction time of 24 hours produced a 46% improvement on Mg^{2+} extraction relative to the baseline. The work of Kosuge et al. provides a possible explanation; the difference between 3*M* sulfuric acid vs. 4 or 5*M* acid concentrations translates to three or five times the amount of reaction time, respectively [30]. The milder acid concentrations investigated in this project may have likely required greater reaction times (24 hours instead of six) to illustrate a time dependency.

Serpentine is a phyllosilicate mineral, consisting of layers of SiO_4^{-4} tetrahedra and $Mg(OH)_6^{-4}$ octahedra. Within the siloxane layers, three oxygen atoms per SiO_4 tetrahedron are shared with adjacent tetrahedral, whereas the octahedral sheets are held together by weak van der Waals bonds [14,38]. Several authors have considered the presence of a silica-rich passive layer during dissolution that may inhibit the further release of magnesium from the serpentine matrix [10,14]. The silica-rich layer may form from either the simple depletion of magnesium from the surface or the deposition of amorphous silica on the serpentine particles. Typically, severe reaction conditions, including strong acids, high temperatures, and extensive comminution, are required if successive layers of $Mg(OH)_6$ are to be exposed. Park et al. have investigated in-situ grinding to continuously expose the magnesium at the surface by physically removing the silica layer [14]. The in-situ grinding was done in the presence of two different reagents, one consisting of 1.4*M* ammonium bisulfate and the second consisting of 1 vol% orthophosphoric acid, 0.9 wt% oxalic acid, and 0.1 wt% EDTA. Although in-situ grinding along showed no additional benefits, the combination of physical and chemical treatments provided for a significant overall improvement in serpentine dissolution.

A three-stage leaching experiment was conducted in an attempt to remove the siloxane layers of serpentine, using a sodium hydroxide treatment. The first stage repeated the baseline conditions mentioned above. The second stage treated the dried solids with 1*M* sodium hydroxide solution, but otherwise with the same solids concentration, reaction time, and temperature as the baseline experiment. The second stage produced 4280 ppm silica while extracting only 7 ppm magnesium. Then the third stage returned to the baseline conditions with 2*M* sulfuric acid. This stage yielded 2200 ppm magnesium, in comparison to the 1830 ppm in the second stage of acid treatment when there is no intermediate base extraction. Although this is an improvement, the quantity of magnesium extracted seems low when considering the amount of silica removed. SEM analysis of the treated solids showed that the magnesium concentration in the surface was notably high, demonstrating that the NaOH treatment effectively removed silica from the serpentine particles and exposed more magnesium [35]. There may be other factors involved besides the passive silica layer inhibiting the dissolution process, since NaOH was able to remove a portion of the silica and expose magnesium, but the magnesium remained in the serpentine matrix much like when the silica-rich layer was intact. The strength of magnesium bonds in the serpentine matrix may be an explanation of the increase in difficulty for the continual removal of ions from a crystal matrix.

Communition of the serpentine particles remains important, because the SEM results support the concept that magnesium is only being removed from the particle surface. The concentration of magnesium in the bulk remained significantly higher than in the surface for each of the samples tested.

An increase in temperature to 50°C yielded a 70% increase in the magnesium dissolution. Although increased temperatures correspond to increased costs, this may likely be outweighed due to larger extraction yields and the corresponding lower volume of minerals required.

4.3. TGA Characterization of Raw and Activated Samples

Removal of the hydroxyl groups present in serpentine minerals increases the chemical reactivity and carbonation efficiencies, probably due to hydroxyl groups inhibiting carbonation by occupying active sites on the serpentine surface [18]. The evolution of these groups is known to occur around 600°C [34]. TGA of the parent sample showed a series of weight losses corresponding to the evolution of adsorbed water, crystallized water, and finally the chemically bound hydroxyl groups. These transitions occur at approximately 120°, 300°, and 500°C, respectively [34]. Sulfuric acid pretreatment was shown to lead to the removal of crystallized water and hydroxyl groups, as indicated by the disappearance or decrease of the TGA transitions at 300 and 500°C.

A statistical evaluation of the TGA data was conducted for the weight loss observed at 800°C. Time does not have a significant role in the increased reactivity of serpentine resulting from acid treatment. A 3*M* acid concentration is clearly preferable to 1.5*M*, but no further gain accrues from increasing the acid concentration to 5*M*.

A set of experiments was conducted with particle sizes of 75–150 μm and >150 μm, and acid concentrations of 1, 1.5, and 4 *M*. The TGA profiles [35] of parent and acid-treated serpentine samples show an initial weight loss of adsorbed water. Further weight losses occurred around 300 and 600°, signaling the loss of water of crystallization and hydroxyl groups, respectively [21]. The strong affinity of sulfuric acid for water can be seen from the fact that increased acid concentrations result in reduced weight losses. In particular, an increase in the removal of hydroxyl groups is evident with an increase in the acid concentration.

Dehydroxylation disrupts the serpentine structure, potentially promoting the carbonation reactivity [19]. It is difficult to determine whether the removal of hydroxyl groups improves dissolution, or whether the removal of hydroxyl is a byproduct of the removal of magnesium. However, work in other laboratories on intensive grinding [17] and heat pre-treatment [29] show that both grinding and heat pre-treatment effectively

target and remove hydroxyl groups, whereupon magnesium is more readily available for carbonation.

4.4. Porous Texture Characterization of Raw and Activated Samples

Previous studies have demonstrated that parent samples with a surface area of 8 m^2/g can be enhanced to nearly 330 m^2/g due to low-temperature dehydroxylation [19,36]. The carbonation of serpentine has been shown to be surface-controlled, as the reaction is limited when the magnesium at the mineral surface is depleted or the surface is inactivated by mass-transfer resistance [31]. Therefore it is assumed that an increase in surface area will promote carbonation.

However, in a series of ten activation treatments, we were not able to replicate the results of ≈300 m^2/g surface areas. Instead, values fell in the range 18–36 m^2/g for all ten of these experiments. The mean value obtained from all ten experiments was 24.48 m^2/g, with a standard deviation of ±5.04 m^2/g.

4.5 Carbonation Studies

4.5.1. Carbon Dioxide Dissolution

The pH of solution is a principal concern, because magnesite becomes vulnerable to dissolution at lower pH values. In addition, there is a pH dependence of the speciation of carbonic acid. Preliminary carbonation studies revealed that the final pH would only narrowly favor the formation of magnesite, and no precipitates were observed. Accordingly, experimentation regarding the dissolution of carbon dioxide and the subsequent drop in pH was carried out.

While the use of sulfuric acid to leach magnesium from serpentine has proven effective, in addition to magnesium in the leachate, iron, aluminum, calcium, and silica are also present. These “impurities” may interfere with the carbonation and potentially confound experimental results. Therefore a simplified system using magnesium sulfate

heptahydrate dissolved in water was used to better understand the Mg^{2+}-CO_2-H_2O system.

Experiments were carried out to evaluate the pH response with and without the addition of a buffer, sodium bicarbonate, and a base, potassium hydroxide. For these experiments the reactor and solution were purged three times at 0.7 MPa and then charged with 0.7 MPa carbon dioxide one final time. Then the air motor and stirrer were started. Pressure stabilization occurred in approximately one minute with the aid of the gas entrainment stirrer. Pressure drop for these experiments equates to the solubility of carbon dioxide. A modest decrease in CO_2 solubility, relative to a control experiment using only water in the reactor, was seen with the addition of the magnesium sulfate or of magnesium sulfate plus sodium bicarbonate. This was attributed to the salting-out effect. An experiment with magnesium sulfate, sodium bicarbonate, and potassium hydroxide all added to the solution resulted in a significant increase in pressure drop, in accordance with Le Chatelier's Principle. The quantity of dissolved CO_2 is increased as the reaction is shifted due to protons from the dissociation of carbonic acid reacting with hydroxide ions from the KOH. If the reactor pressure were to be held constant, the pH would drop as CO_2 continues to go into solution.

Conceivably one could increase magnesium concentration; however, elevated concentrations of magnesium have been shown to hinder the carbonation reaction, and CO_2 becomes the limiting reagent. The use of sodium bicarbonate in the reaction has been established to buffer the pH of solution and consequently control the speciation of bicarbonate and carbonate ions [9]. In otherwise comparable experiments with and without sodium bicarbonate present the final pH values varied from 6.66 with bicarbonate to 4.93 without it [35].

4.5.2. Carbonate Formation

No crystallization occurred inside the reactor for reaction times up to 72 hours, which was in agreement with correspondence from the National Energy Technology Laboratory [32]. NETL reported that no solid precipitate was present on immediately

removing the sample from the reactor, but in letting the liquid filtrate stand overnight some precipitate did appear. We observed the same pattern. One possible explanation is that crystallization kinetics are such that precipitation requires longer times than were allotted in the reactor. A second possibility is that magnesium is reacting with atmospheric carbon dioxide dissolving into solution, since the beakers remain open to the atmosphere after removal from the reactor. A third explanation is that the magnesium ions are reacting with the buffer, sodium bicarbonate.

To sort this out, experiments were carried out to investigate the effects of sodium bicarbonate and potassium hydroxide on the carbonation of magnesium. After one month, an experiment with no bicarbonate or hydroxide showed no conclusive carbonation, whereas experiments with added sodium bicarbonate or sodium bicarbonate plus potassium hydroxide all formed precipitates, each of which contained sodium bicarbonate. X-ray diffraction showed that the precipitates are a hydrated magnesium carbonate, nesquehonite. The addition of sodium bicarbonate beyond the stoichiometric requirement improved the mass of product by about 30%.

To draw some further comparisons, the following carbonation experiments were carried out, all of which used only magnesium sulfate in solution (i.e., no added bicarbonate or hydroxide): First, two experiments, one run for 15 minutes and the other for 24 hours, but both at ambient temperature. After the respective solutions were transferred to a fume hood and allowed to stand, even after twenty days neither showed any precipitation. A second pair of experiments was run at 72 hours, but one at 10°C and the other at 70°C. Neither had any noticeable precipitation upon removal from the reactor. However, the solution from the 70°C experiment showed definite precipitation after standing for one week, whereas the experiment run at 10°C took 19 days.

Two experiments were run with 200 mL of water and 12.03 g $MgSO_4 \cdot 7H_2O$, but one was at 4 MPa CO_2 pressure and the other at 0.7 MPa. The final pH for both solutions was 3.9. The concentration of bicarbonate ions was 0.0051*M* in the higher-pressure experiment, compared to 0.00077*M* for the lower-pressure run. It is immediately clear

that an external control on the pH is needed or an alternate route needs to be taken. The bicarbonate/carbonate ion concentration can be augmented with the addition of a base such as potassium hydroxide. However, the consumption of an additional reagent (i.e., KOH) will have a negative impact on process economics.

4.5.3. Thermodynamics of the Mg-CO_2-H_2O System.

The dissolution of serpentine can be facilitated by extreme conditions, however the carbonation of magnesium ions requires a balanced set of reaction conditions. Thermodynamic relations are able to provide a framework for these carbonation reaction parameters. Reaction kinetics then further develop the understanding of the Mg-CO_2-H_2O system by taking into account the magnesium ion as an aquo-ion, with the hydration of the magnesium ion leading to metastable products.

Acidic conditions facilitate the removal of magnesium from the antigorite matrix. However, carbonates are also susceptible to dissolution at lower pH levels via the protonation of surface carbonate groups. The stability of magnesite can be more easily visualized by the diagram in Figure 1.

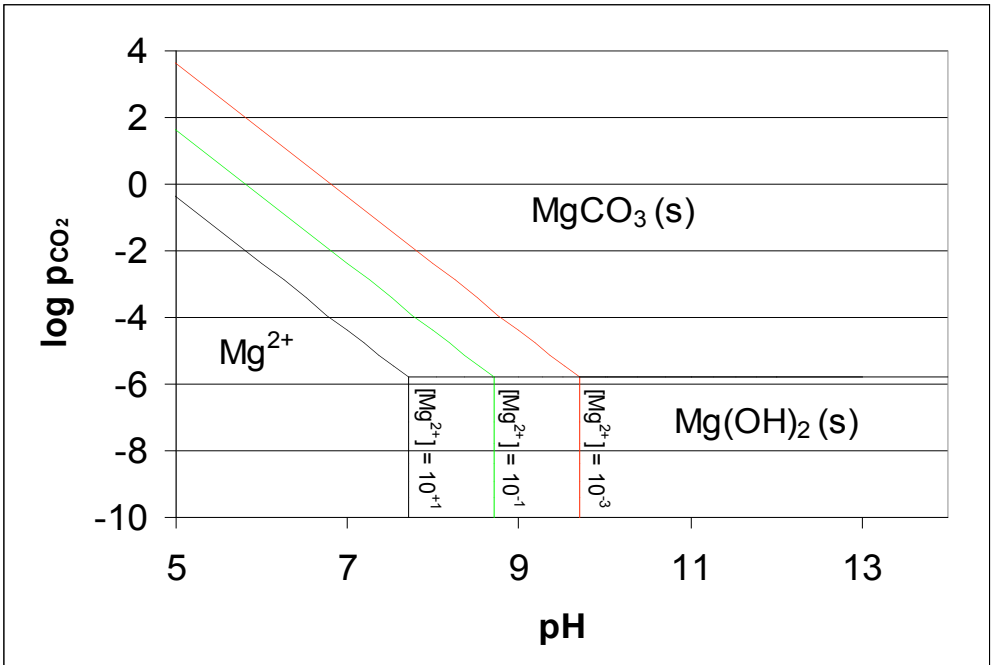

Figure 1. Stability diagram of magnesite according to pH and CO_2 pressure

The dissolution of gaseous carbon dioxide in aqueous solution proceeds according to Reaction 1 with the hydration of carbon dioxide to form carbonic acid (Reaction 2), which then may dissociate into bicarbonate and carbonate ions (Reactions 3 and 4, respectively).

$$CO_2(g) \leftrightarrow CO_2(aq) \qquad \text{Reaction 1}$$

$$CO_2(aq) + H_2O \leftrightarrow H_2CO_3 \qquad \text{Reaction 2}$$

$$H_2CO_3 \leftrightarrow HCO_3^- + H^+ \qquad \text{Reaction 3}$$

$$HCO_3^- \leftrightarrow CO_3^{2-} + H^+ \qquad \text{Reaction 4}$$

The crystallization of magnesite is favored with increasing P_{CO2} and pH, however these two reaction variables are intrinsically tied. The dissolution of carbon dioxide (g) and formation of carbonic acid is increased with increasing P_{CO2}, resulting in a pH drop due to the dissociation of carbonic acid. In conjunction with thermodynamic calculations, the pH of an aqueous solution is illustrated in Figure 2 according to the partial pressure of CO_2 (g). Close inspection of the inset plot in Figure 2 reveals a P_{CO2} of approximately 1000 atm (105 MPa) favors the presence of magnesite over magnesium

ions. However our empirical evidence has suggested a moderate P_{CO2} might be preferred as the carbonation reaction occurs overnight as the solution equilibrates with atmospheric pressures.

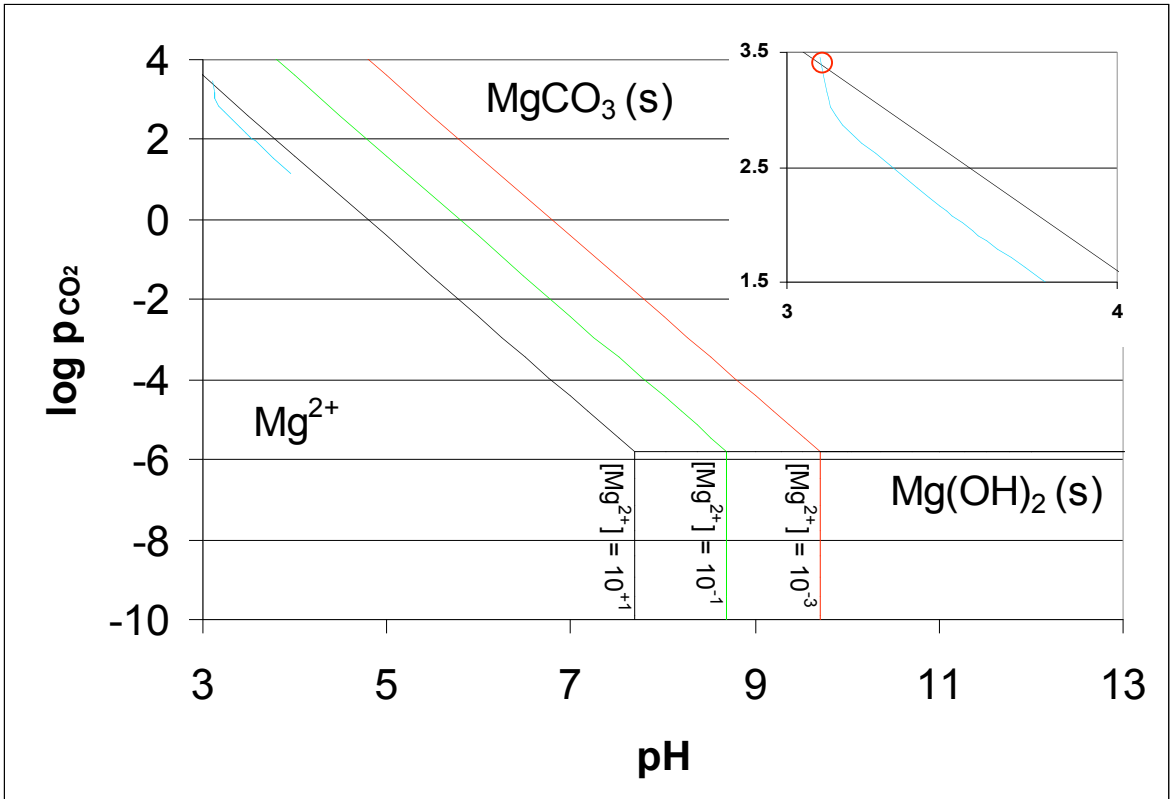

Figure 2. Magnesite stability diagram overlain with the P_{CO2} vs. pH relationship

The crystallization process can be divided into three stages: supersaturation, nucleation, and crystal growth. For a given reaction to move toward the formation of precipitates, a degree of supersaturation needs to be achieved. Although Figure 2 highlights a set of conditions suitable for the presence of $MgCO_3$, it does not provide for the required degree of supersaturation. The formation of carbonates may occur when the ion activity product is greater than the solubility product. However, conditions well in excess of saturation are required for crystallization of magnesium carbonates. In addition to a required degree of supersaturation, the existence of metastable products also precludes the crystallization of magnesite at these conditions.

The formation of magnesite has been shown to be more dependent on the concentration of carbonate ions than on the magnesium ion concentration. Higher concentrations of magnesium ions, although increasing the reaction quotient, have empirically shown to not aid in the formation of magnesite. Therefore, focusing on the concentration of carbonate/bicarbonate ions in solution provide a better measure of the carbonation potential of the solution.

The formation of carbonates may occur when the ion activity product is greater than the solubility product. However, conditions well in excess of saturation are required for crystallization of magnesium carbonates. In addition to a required degree of supersaturation, the existence of metastable products also precludes the crystallization of magnesite at these conditions.

Magnesite is the thermodynamically stable reaction product between magnesium ions and carbonate or bicarbonate ions in aqueous solution. However, the hydration of the magnesium ion kinetically favors the formation of hydrated magnesium carbonates, nesquehonite and hydromagnesite. Accordingly, the diagram has been redrawn in Figure 3 with respect to nesquehonite. It can be seen that there is no overlap between the stability region of nesquehonite and the pressure/pH relationship pertaining to the dissolution of $CO_2(g)$. The partition between $MgCO_3$ and $MgCO_3 \cdot 3H_2O$ is denoted by a dashed line to signify that magnesite is the stable product, however nesquehonite may be kinetically favored within this region. Initially the parallel stability regions for magnesite and nesquehonite appear suspicious, however the diagram is based on thermodynamic data. As such, the only difference between magnesite and nesquehonite in terms of the stability diagram is the values for the Gibbs free energy of formation, as the three water molecules for nesquehonite do not factor into the calculations.

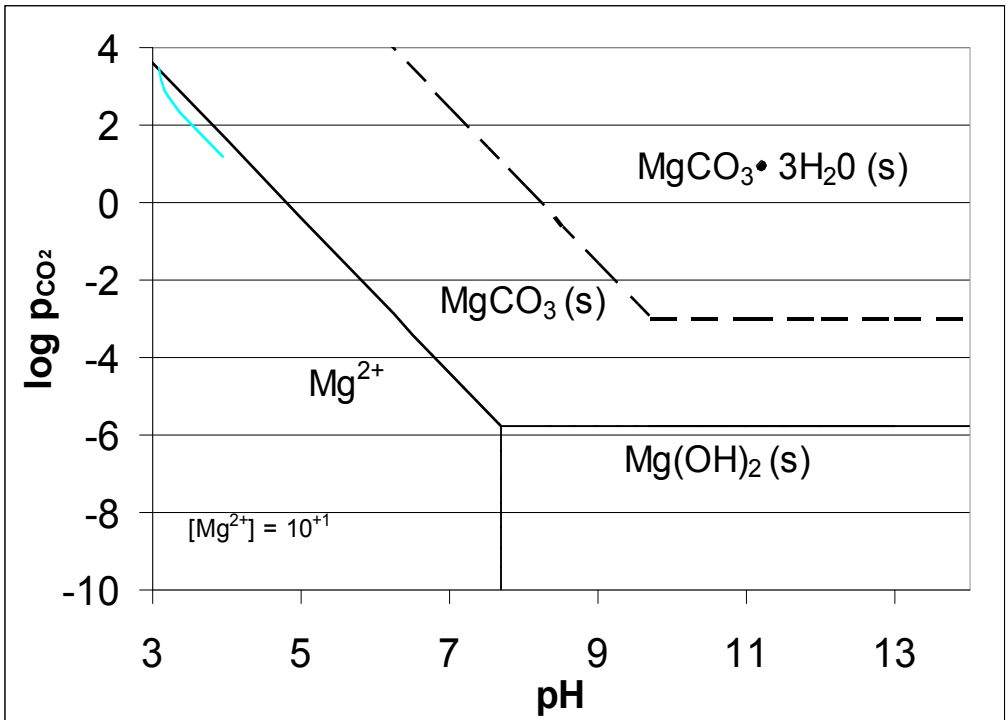

Figure 3. Stability diagram of magnesite and nesquehonite

Although the dissolution of carbon dioxide and the resultant pH are in close proximity with respect to the stability of magnesite, they remain significantly removed from the stability of nesquehonite. The formation of magnesite is desirable because its solubility ($Ksp=10^{-8.1}$) is three orders of magnitude less than nesquehonite ($Ksp\approx10^{-5}$). In addition, the quantity of CO_2 sequestered per unit volume is reduced with increasing water content, i.e. more space will be required for storing hydrated magnesium carbonates.

4.5.4. Carbonation of a Titrated, Serpentine Leachate, and Model Solutions

The use of sulfuric acid to leach magnesium from serpentine has proven effective [27]. The magnesium ions are present in aqueous solution for carbonation. The titration of the serpentine leachate (3*M* H_2SO_4 reacted with 50 g of serpentine for 3 hours at room temperature) with sodium hydroxide was done drop-wise from a pH of –1 to 13.5. In addition to the dissolution of magnesium during the leaching stage, additional metals, such as iron, calcium, manganese, and aluminum, are also dissolved because they are

present in the form of accessory minerals or as cations substituted in the serpentine structure. A benefit of the titration stage is the additional removal of iron as precipitated, amorphous iron (hydr)oxides which occurs at a a near-neutral pH. Iron(II) (and dissolved iron(III) upon reduction to iron(II)) can react with carbon dioxide, forming siderite, which is also stable under ambient conditions. However, metallic impurities such as iron, manganese and aluminum are often associated with an interference of the crystallization process [31].

The pH of solution is a principal factor in the speciation of carbonic acid, but in addition carbonates become increasingly vulnerable to dissolution at lower pH values, as shown in Figures 1, 2, and 3. Experiments 1 and 2, as presented in Table 1, were conducted as preliminary carbonation studies. It should be noted that pH_o corresponds to the pH prior to pressurization of the reactor and pH_f corresponds to the pH immediately after depressurization. These experiments reveal that the final pH would only narrowly favor the presence of magnesium carbonates. Consequently no precipitates were observed. As the degree of saturation was calculated to be only slightly greater than 1, it is not surprising that precipitates were not observed. Preliminary experimentation indicates that a degree of saturation of 5 is required for the precipitation of magnesium carbonates to occur. This is in good agreement with a degree of saturation between 1.8 and 13.8 for the precipitation of magnesite. Accordingly, experimentation and calculations focusing on increasing the pH and the carbonate/bicarbonate ion concentration were carried out.

Table 1. Experimental Conditions for Carbonation of Serpentine Leachate

	H_2O, mL	$MgSO_4$	$NaHCO_3$	KOH	P_{CO2}, MPa constant	pH_o	pH_f	Temp ^oC	Time hrs
Experiment 1	146	0.1*M*	--	--	4.6	13.04	7.15	Room	24
Experiment 2	200	0.1*M*	--	--	4.6	13.50	7.44	Room	6

As previously mentioned, the concentration of carbonate and bicarbonate ions is intrinsically related to the pH and is fundamental to the carbonation reaction. In addition, metallic impurities such as iron, manganese, and aluminum may interfere with the carbonation testing and potentially confound experimental results. Therefore, a simplified solution using magnesium sulfate heptahydrate and sodium bicarbonate as the precursor has been used in these experiments to better understand the Mg-CO_2-H_2O system under ambient conditions (Table 2).

Having previously established the ability to leach magnesium from serpentine and into aqueous solution, attention is turned to (1) the concentration or, more specifically, the activity of carbonate and bicarbonate ions and (2) the subsequent reaction of these anions with magnesium ions. The activity of carbonate and bicarbonate ions is dependent on the dissolution of CO_2 (g) and the pH of solution. Previous researchers have utilized buffers such as sodium bicarbonate, and bases such as potassium or sodium hydroxide, to adjust the pH and therefore control the speciation of carbonic acid [32]. Accordingly, experimentation was carried out with distilled water and various reagents using the Parr reactor, under CO_2 pressures ranging from 0.35 to 3.8 MPa. These experiments were conducted in the Parr reactor with an initial P_{CO2} charge of 0.7 MPa. The experiments were then run until the dissolution of CO_2 (g) was equilibrated. The dissolution of CO_2 (g) required 2–2.5 minutes, which is in good agreement with kinetic calculations for the rate-limiting step of Reaction 2. Since the CO_2 was supplied as a one-time charge rather than from an infinite reservoir, the final pressure relates to the solubility of CO_2. A modest decrease in the CO_2 solubility can be seen in Table 2 with the addition of reagents for experiments 8 and 9 versus experiment 7, which can be attributed to the salting-out effect [39]. As the ionic strength is increased the competition for chemical species, neutral species in particular, to coordinate with water molecules also increases, thereby reducing the solubility of CO_2(g). Experiment 10 resulted in a significant increase in the pressure drop, in accordance with Le Chatelier's Principle. The quantity of dissolved CO_2(g) is increased as Reactions 1-4 shift to the right due to the consumption of protons by hydroxyl groups, forming water. Experiment 8, carried out with 0.1*M* magnesium sulfate heptahydrate, 200 mL reverse- osmosis water, and an initial pressure of 0.7 MPa

(final pressure of 0.3 MPa), demonstrated a pH level (4.05) and bicarbonate/carbonate ion concentration ($10^{-3}M$) insufficient for producing magnesium carbonates. Consequently, experiments were carried out with the addition of a base, potassium hydroxide, to improve the thermodynamics for the formation of magnesium carbonates. Even with an otherwise similar solution but containing 0.5*M* KOH, the final pH of 6.50 remained too low for immediate carbonation. Although the pH of solution prior to carbonation is elevated, the presence of a base increases the quantity of CO_2(g) that is dissolved within the solution. This leads to an increase in the bicarbonate/carbonate ion concentration. However, the increased dissolution of carbon dioxide also leads to a decrease in pH, thereby tempering the increase in carbonate and bicarbonate ion concentration.

Table 2. CO_2 Experimental Conditions for CO_2 Solubility Tests.

	H_2O, mL	$MgSO_4$	$NaHCO_3$	KOH	P_{CO2}, MPa Initial*	P_{CO2}, psi Final*	pH_o	pH_f	Temp ^oC
Experiment 7	200	--	--	--	0.7	39	6.45	5.20	Room
Experiment 8	200	0.1*M*	--	--	0.7	42	6.39	4.05	Room
Experiment 9	200	0.1*M*	0.5*M*	--	0.7	43	7.60	6.70	Room
Experiment 10	200	0.1*M*	0.5*M*	0.1*M*	0.7	1	10.19	9.13	Room

*P_{CO2} Initial is the pressure inside the reactor at the beginning of the experiment and P_{CO2} Final is the stabilized pressure after the solution has equilibrated

To achieve a degree of supersaturation, the magnesium concentration can be increased, but elevated concentrations of magnesium have shown to hinder the carbonation reaction and CO_2 being the limiting reagent. Consequently, the focus centered on the carbonate and bicarbonate ion activity. The use of sodium bicarbonate in the carbonation reaction has been established to buffer the pH of solution and consequently control the speciation of bicarbonate and carbonate ions [32]. Experiments 11 and 12 were carried out to better understand the effectiveness of sodium bicarbonate

as a buffer (Table 3). The final pH values for the solutions varied from 6.66 with the sodium bicarbonate (experiment 11) to 4.93 without sodium bicarbonate (experiment 19). The bicarbonate ion concentration for experiment 18 was calculated to be 1.97 *M* (not including the bicarbonate ions from the sodium bicarbonate) and just .037 *M* for experiment 12.

Table 3. Experimental Conditions Investigating the Buffering Capacity of $NaHCO_3$ with CO_2 (g)

	H_2O, mL	$MgSO_4$	$NaHCO_3$	KOH	P_{CO2}, MPa Initial	P_{CO2}, MPa Final	pH_o	pH_f	Temp ^oC
Experiment 11	200	--	0.1*M*	--	2.8	1.46	8.06	6.66	Room
Experiment 12	200	--	--	--	2.8	1.52	7.06	4.93	Room

Although bicarbonate and carbonate ion concentrations are adequate with the addition of a buffer or base, the formation of carbonates still seems to be suppressed inside the reactor, because XRD tests and elemental analysis do not show conclusive evidence of carbonates. No crystallization has been found to form inside the reactor (times up to 72 hours), which is in agreement with correspondence from NETL [32]. NETL reported that, in their tests, no solid precipitate was present upon immediately removing the sample from reactor. However, in letting the liquid filtrate stand overnight, some precipitate did appear. The appearance of crystals during our experimentation has followed a similar pattern. A possible explanation would be that the reaction kinetics are such that precipitation requires longer reaction times than were allotted in the reactor. A second possibility is that the magnesium is reacting with atmospheric carbon dioxide dissolving into solution, because the beakers remain open to the atmosphere upon removal from the reactor. A third possibility is that the pH and the activity of carbonate and bicarbonate ions is too low, resulting in a degree of saturation insufficient for precipitation of magnesium carbonates. Accordingly, experimentation was conducted to narrow down the inhibiting factor(s) for the carbonation of magnesium ions.

The difficulty in forming carbonates inside the reactor is a significant issue, because the alternative means of carbonation requires several days. Experiments 13-16, shown in Table 4, were conducted over the course of one month to determine if the activation energy was such that longer reaction times are required. These experiments were also left open to the atmosphere, since the solubility of atmospheric CO_2 may be responsible for carbonation. Finally, experiments were conducted with varying concentrations of potassium hydroxide and sodium bicarbonate to affect pH and the concentration of carbonate and bicarbonate ions. Although the ambient concentration of CO_2 is only about 370 ppm, the solubility of the gas may be responsible for the formation of carbonates in containers left open to atmospheric conditions overnight. After one month, experiment 13 showed no conclusive carbonation, whereas experiments 14, 15, and 16 all formed precipitates, each of which contained sodium bicarbonate. This strongly suggests that carbonation is due to the addition of sodium bicarbonate. It is suggested that a future project could utilize $NaHC^{13}O_3$ to precisely track the source of the carbonate or bicarbonate ions.

Table 4. Experimental Conditions to Determine the Factors Affecting Carbonation

	H_2O, ml	$MgSO_4$	$NaHCO_3$	KOH	P_{CO2}	Temp ^oC
Experiment 13	400	.1M	--	--	atm	Room
Experiment 14	400	.1M	1M	--	atm	Room
Experiment 15	400	.1M	.5M	.1M	atm	Room
Experiment 16	400	.1M	.5M	--	atm	Room

XRD results in Figure 6 show that the precipitates are a hydrated magnesium carbonate, nesquehonite, with SEM images of the crystals shown in Figures 7 and 8. These figures highlight the variation in crystal size due to pH and the subsequent crystallization time. Although the composition is identical, the morphology is different due to crystallization times. An increase in pH for experiment 15 led to a higher concentration of carbonate and bicarbonate ions, which increases the degree of saturation. Accordingly the formation of crystals is fast relative to experiment 14, resulting in smaller crystals for experiment 15. These experiments also demonstrated that the

addition of sodium bicarbonate beyond the stoichiometric requirement improved the mass of product by about 30%.

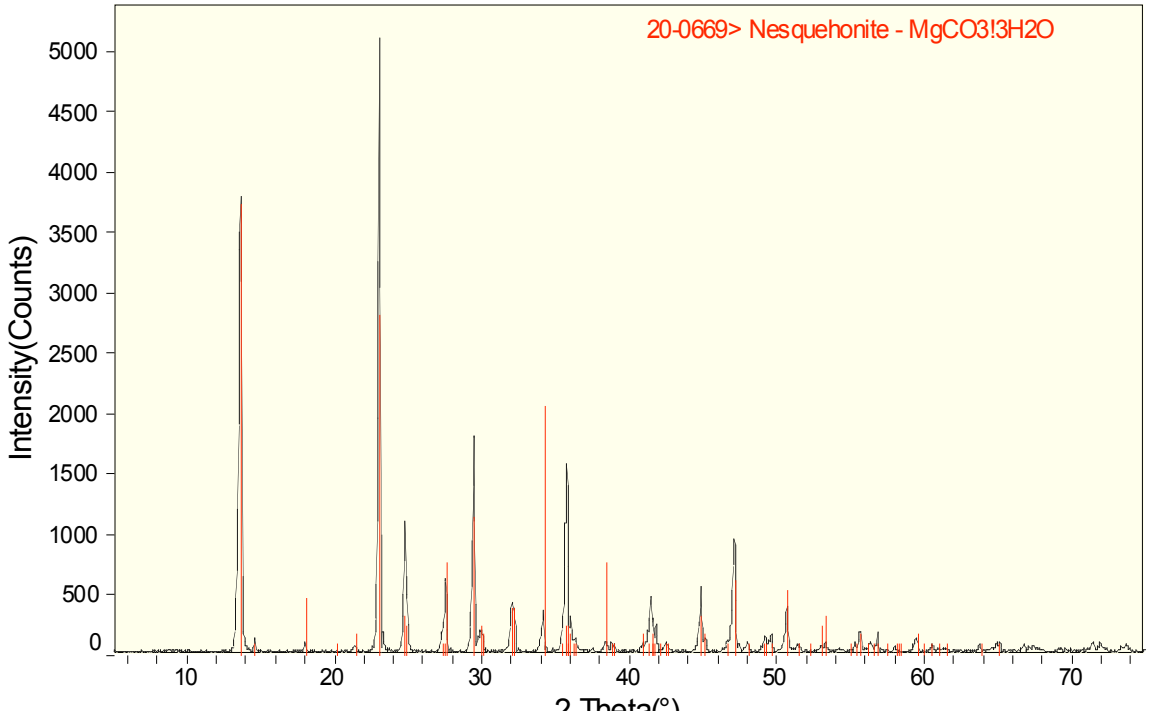

Figure 6. XRD result for experiment 14 showing the hydrated magnesium carbonate, nesquehonite

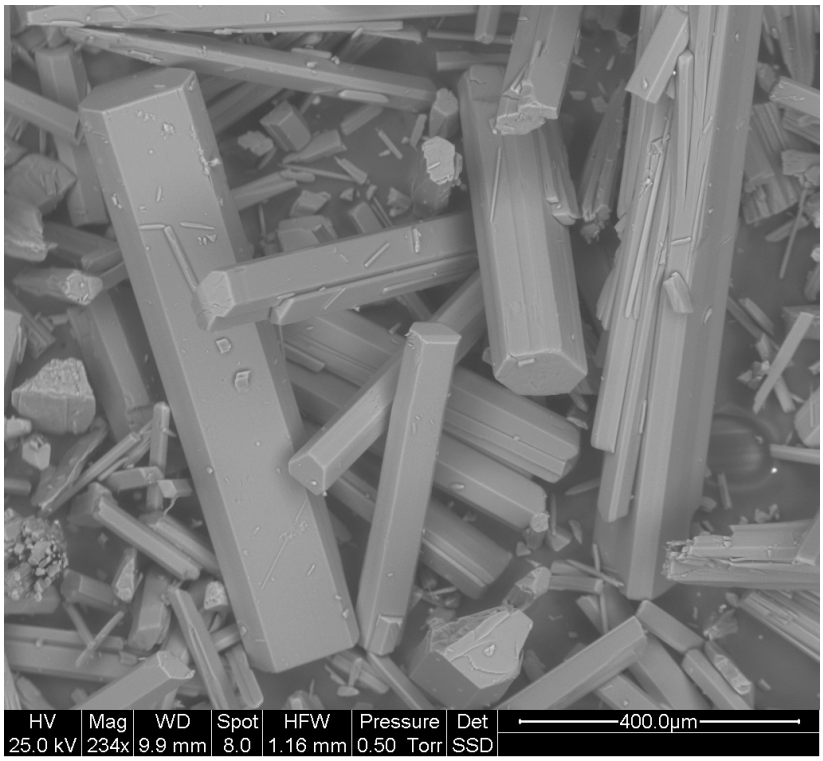

Figure 7. SEM image of nesquehonite crystals from experiment 14.

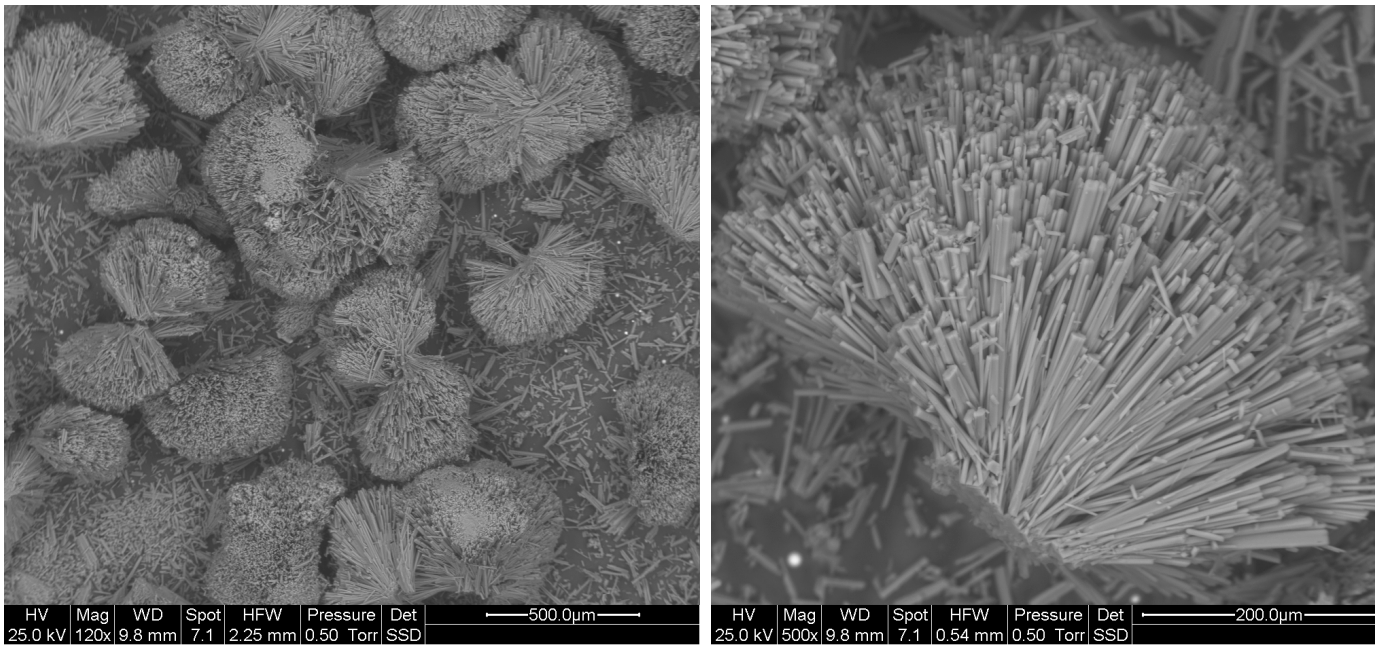

Figure 8. SEM image of nesquehonite crystals with the addition of potassium hydroxide (experiment 17).

The pH of solution is a fundamental parameter to producing carbonates and the scale of potential industrial applications for mineral carbonation prohibits the consumption of a base or the use of sodium bicarbonate as a "buffer," since it preferentially reacts with Mg^{2+} over CO_2(g). Referring to Figure 3, the P_{CO2}/pH trend shows the limitation of forming magnesium carbonates without any additional reagents. Experiments 17 and 18 were conducted with magnesium sulfate heptahydrate and confirm the difficulty in precipitating magnesium carbonates, based solely on the final pH of solution (Table 5). Therefore the use of serpentine has been considered as a potential buffering against the dissolution of carbon dioxide.

Table 5. Experimental Conditions for Determining the pH in the Mg-CO_2-H_2O system.

	H_2O, mL	$MgSO_4$	$NaHCO_3$	KOH	P_{CO2}, MPa constant	pH_o	pH_f	Temp ^oC
Experiment 17	200	.1M	--	--	4	6.3	3.9	Room
Experiment 18	200	.1M	--	--	0.7	6.3	3.9	Room

Experiment 19 was conducted as an initial investigation into the buffering capacity of serpentine. At a P_{CO2} of 3.9 MPa the final pH was 6.58 compared to experiments 17 and 18, which were conducted at pressures of 4 and 0.7 MPa respectively with a corresponding pH of 3.9. The bicarbonate ion concentrations for experiments 17 and 18 were calculated to be 0.005*M* and 0.000 *M* respectively, whereas the bicarbonate ion concentration for experiment 87 was 2.25*M*. It was also found that a precipitate, presumably nesquehonite, formed within 24 hours under ambient conditions. So, not only was serpentine capable of buffering a carbonic acid solution, magnesium was able to be leached out.

Some researchers have favored the use olivine rather than serpentine due to its greater solubility, however the addition of consumable reagents has been used for both magnesium silicates [33]. Experiment 20 tested the effectiveness of olivine for the

capture of carbon dioxide (Table 6). The pH_f of solution immediately upon venting was 5.47 and as no precipitate was formed, so additional reagents appear to be required.

Table 6. Experimental Conditions for Buffering Capacity of Serpentine and Olivine

	H_2O, mL	Serpentine, g	Olivine, g	P_{CO2}, MPa	pH_o	pH_f	Temp ^oC	Time hrs
Experiment 19	100	13.8	--	3.8	7.18	6.58	Room	2
Experiment 20	100	--	13.8	3.8		5.47	Room	2

The dissolution of serpentine is the underlying strategy for the production of magnesium carbonates in a one-stage process. The use of a swing process such as described in Park and Fan [14] promotes the carbonation conversion but the consumption of reagents renders the process economically unrealistic. Ideally, the dissolution of serpentine and crystallization of magnesium carbonate products would be carried out under identical conditions. Although the feasibility is improved by stepping back to the original one-stage process, the focus needs to readdress the rate-limiting step of magnesium removal. A potential pathway that could be investigated in a future project is the use of microwave technology, which has the ability to uniquely target and weaken the antigorite structure due to the inherent moisture content.

5. CONCLUSIONS

The overall objective of the program was to optimize the active carbonation process, in order to design an integrated CO_2-sequestration module. Chemical activation by sulfuric acid treatment, has proven to be effective for increasing the reactivity of serpentine.

Particle-size reduction to a D_{50} ≤125 μm is necessary for enhancement of dissolution. An increase in acid concentration leads to an increase in the mass loss from serpentine. As verified by ICP, these mass losses are primarily due to magnesium dissolution. At the same time, there is an increase in surface reactivity through the removal of hydroxyl groups. TGA results indicate that acid concentrations ≥3*M* are favorable, with the particle size at a D_{50} of 125 μm being ideal. Reactions are indifferent to variations in reaction time. Surface area results were significantly lower than expected.

The treatment of serpentine with sulfuric acid has been shown to be effective in the leaching of magnesium for its subsequent carbonation. In this work, reaction conditions were maintained under a milder regime to assess the relative contribution of several reaction variables—acid concentration, particle size, and reaction time—on the dissolution process. Although the effects of time are too slight to appear within shorter time periods, a 24-hour reaction was shown to provide a 46% improvement in the extraction of Mg^{2+}. The effects of increased reaction temperature, from 25°C to 50°C, provided a 70% improvement in dissolution. Additionally, multi-stage leaching provided little gain in Mg^{2+} extraction, whether it was a two-stage acid leaching, or two stages of acid leaching with one stage of base leaching in between.

In contrast to the dissolution process, where extreme conditions are favored, the carbonation reaction requires a more careful balance of reaction variables. Magnesite, although stable under ambient conditions, is vulnerable to dissolution in an acidic environment. Initial investigations revealed that a partial pressure of 4.6 MPa resulted in conditions too acidic for the formation of magnesium carbonates, regardless of the

addition of a base. Further, the bicarbonate ion concentration remains two orders of magnitude too low without the addition of a buffer such as sodium bicarbonate, even at lower partial pressures. In addition, experimentation was able to show that it is sodium bicarbonate that is responsible for the formation of carbonates.

Thermodynamic relations provide the range of theoretically favorable reaction conditions for the precipitation of magnesite. However, at these conditions kinetics dictate the predominance of metastable phases over the stable phase, magnesite. Electrostatic interactions between the magnesium ions and water molecules lead to a stable solvation shell [40,41]. Consequently, the requisite interactions between magnesium ions and carbonate ions are inhibited, leading to prolonged carbonation times and metastable products such as nesquehonite, hydromagnesite, and lansfordite.

The stable hydrated magnesium ion can be affected so as to promote ligand exchange. Increased reaction temperatures can reduce the hydration number and increase the water exchange rate, both of which improve the chances of bicarbonate or carbonate ions interacting with magnesium ions [40,42,43]. Also improving these interactions is the addition of NaCl, reducing the volume of water required to equalize the electronegativity of the magnesium ions [44-46]. The production of magnesite may not be kinetically favored; however, the kinetic limitations may be overcome or at least reduced somewhat by carefully targeting the waters of hydration.

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7. ABBREVIATIONS AND ACRONYMS

AES	atomic emission spectroscopy
atm	atmospheres, atmospheric
BET	Brunauer, Emmet, and Teller
°C	degrees Celsius
D_{50}	median particle size
EDTA	ethylenediaminetetraacetic acid
g	grams
ICP	inductively coupled plasma
K	kelvins
kWh	kilowatt-hours
L	liters
LOI	loss on ignition
m	meters
M	molar (concentration)
mL	milliliters
mm	millimeters
MPa	megapascals
NETL	National Energy Technology Laboratory
P	pressure
P_0	saturated vapor pressure
ppm	parts per million
SEM	scanning electron microscopy, microscope
TGA	thermogravimetric analysis
XRD	X-ray diffraction
μm	micrometers (microns)